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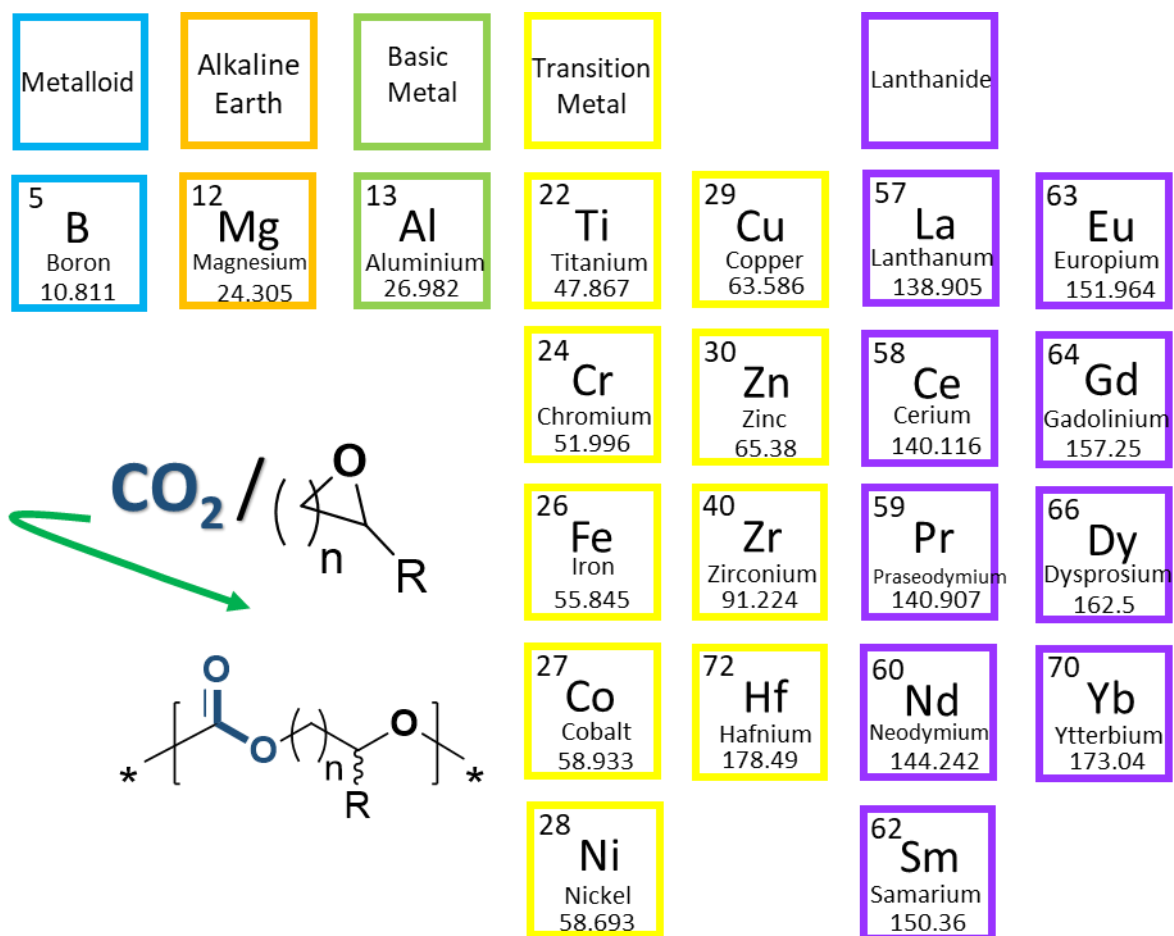
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# Update and challenges in CO<sub>2</sub>-based polycarbonate synthesis

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## 1.1 Introduction

Over the past century, plastics have revolutionised the industrial sector by allowing for the replacement of natural building blocks, such as metal, wood and stone, with cheaper, more durable and adaptable synthetic materials.<sup>[1]</sup> Although the continued development of plastics industry has revolutionized many sectors including automotive, healthcare, electronics and packaging, the environmental stress of producing and disposing of such materials is acutely apparent.<sup>[2]</sup> Currently, the majority of consumer plastics are manufactured from petroleum derived sources, and the abuse of such fossil fuels is accelerating carbon dioxide (CO<sub>2</sub>) emissions, leading to a warmer, more unstable, global environment.<sup>[3]</sup> As such, there is substantial incentive to diversify the plastics industry by producing materials with lower environmental impact. Currently, polyesters such as poly(lactic acid) (PLA) or poly(butylene succinate) (PBS) account for a substantial proportion of the global production capacity of biodegradable plastics.<sup>[4]</sup> However, polycarbonates, which can be

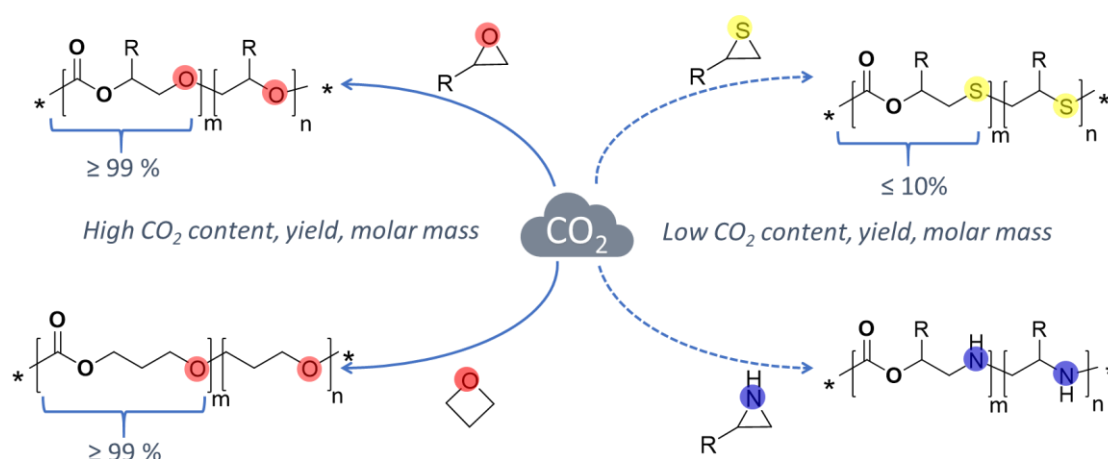
prepared using CO<sub>2</sub> as a comonomer, have been noted for their biodegradability and diverse properties and thus could become an increasingly useful sustainable plastic.<sup>[5]</sup>

Compared to the highly reactive carbon monoxide (CO), both the fully oxidised state and centrosymmetric structure of CO<sub>2</sub> renders it relatively inert. However, the presence of the two electronegative oxygen atoms confers a somewhat electrophilic behaviour to the carbon atom, making it susceptible to undergoing nucleophilic attack.<sup>[6]</sup> From a purely chemical perspective, CO<sub>2</sub> is a sustainable, bio-renewable, non-toxic and non-flammable C1 feedstock that could be valorised in a variety of chemicals. These include small molecules, such as carboxylic acids, cyclic carbonates, methanol, or longer hydrocarbon chains (C5-C11)<sup>[7]</sup> as well as polymeric structures. Hence efforts have been directed towards CO<sub>2</sub> homopolymerization to produce poly(CO<sub>2</sub>).<sup>[8]</sup> While direct polymerisation is possible, requiring formidably high temperature and pressure ( $4 \times 10^4$  MPa, 1800 K)<sup>[9]</sup>, the process is entropically disfavoured, converting ineluctably poly(CO<sub>2</sub>) into CO<sub>2</sub> gas under normal temperature conditions and lower pressure. For these reasons, using CO<sub>2</sub> as a comonomer remains the only practical approach to incorporating CO<sub>2</sub> into polymer structures.

To prepare CO<sub>2</sub>-based copolymers, two techniques have been developed. The first consists of preparing a CO<sub>2</sub>-based monomer followed by a polymerization process (“monomer to polymer” technique, M to P), and the second entails a direct “chain up” process of the CO<sub>2</sub> with other comonomers. The “M to P” technique provides a wide range of polymer precursors<sup>[10]</sup> and offers the advantage of using sublimed dry ice as a CO<sub>2</sub> resource. In contrast, by-products and uneconomical purification processes are generally involved in this time-consuming approach.<sup>[10c]</sup> As far as the CO<sub>2</sub> “chain up” technique is concerned, polycondensation and ring-opening copolymerization (ROcP) have been used and reported. The polycondensation methodology allows various products to be prepared through the copolymerization of CO<sub>2</sub> with corresponding substrates, such as diols,<sup>[11]</sup> diamines, and dihalides.<sup>[11-12]</sup> However, uncontrollable polymerization presents some drawbacks, and

these, along with the concomitant by-products, plague the development of such a method for potential industrial applications.

The ring-opening copolymerization of CO<sub>2</sub> with heterocycles presents a desirable route to access polycarbonates<sup>[13]</sup> since only a few small molecule by-products are produced in a controlled manner. Typically, three or four-membered heterocyclic molecules (HC) which feature high ring strain, such as epoxide (EP), oxetane, episulfide (ES) or aziridine (AD), are suitable comonomers in CO<sub>2</sub>-based ROcP. The driving force of the process is then entirely based on the cleavage of the C-X (X = N, O, S) bond, which depends on the nature of the heterocyclic molecule ring strain energy ( $E_r$ ). As compared to the other comonomers, episulfide possesses the lowest  $E_r$  value ( $\sim 17.7 \text{ kcal}\cdot\text{mol}^{-1}$ ),<sup>[14]</sup> which considerably reduces its reactivity with CO<sub>2</sub>.<sup>[15]</sup> However, epoxide ( $E_r = 27.2 \text{ kcal}\cdot\text{mol}^{-1}$ ),<sup>[16]</sup> oxetane ( $E_r = 24.8 \text{ kcal}\cdot\text{mol}^{-1}$ )<sup>[17]</sup> and aziridine comonomers ( $E_r = 26 \sim 27 \text{ kcal}\cdot\text{mol}^{-1}$ )<sup>[18]</sup> are sufficiently reactive to theoretically expect a “chain-up” process with CO<sub>2</sub> (Scheme 1). Despite the high ring strain of aziridines, the main drawback of a CO<sub>2</sub>/AD copolymerization, along with the issue of the CO<sub>2</sub>-catalyzed homopolymerization of aziridine<sup>[19]</sup>, is the formation of non-productive carbamic acid species. This results in an uncontrollable copolymerization with the appearance of cyclic side-products and some branched copolymer structures.<sup>[20]</sup> Hence, the copolymerization of CO<sub>2</sub> with epoxide and oxetane to form aliphatic polycarbonates represents the best and most common route to prepare polymers, due to the high reactivity and chemical tunability of the oxygen heterocycles (Scheme 1).<sup>[21]</sup>



**Scheme 1.** General characteristics of the copolymerization of CO<sub>2</sub> with ring-strained heterocyclic monomers.

Only a few oxetane/CO<sub>2</sub> coupling studies have been reported<sup>[22]</sup> and this is likely due to the relative higher cost and lower inherent reactivity of oxetanes as compared to oxiranes.<sup>[23]</sup> Consequently, CO<sub>2</sub>/EP copolymerizations have been studied extensively, not only for the superior ring-opening activity of epoxides, but also for the more economical synthesis of epoxides based on petroleum<sup>[24]</sup> and/or biological starting materials.<sup>[25]</sup>

There are two recent reviews that have highlighted some metal catalysts used for CO<sub>2</sub>-derived polycarbonate synthesis with the first focusing on functional polycarbonates<sup>[26]</sup> and the latter excluding Mg, Cu and metal-centered catalysts.<sup>[27]</sup> The present review will focus on the progress realised in the preparation of cyclic carbonate synthons and aliphatic polycarbonate preparation from CO<sub>2</sub>/EP copolymerizations. Furthermore, it is considered comprehensive for all metal-based processes and includes the rapidly developing field of organocatalytic approaches. Currently the field is still considered young, since the first example of copolymerization dates back to 1969,<sup>[28]</sup> and the early work of Baba *et al.* on oxetane/CO<sub>2</sub> copolymerization was only reported in 1984.<sup>[29]</sup> Today the field is rapidly expanding with primary developments encompassing polycarbonate syntheses under increasingly mild (and more economical) conditions which should place these materials at the forefront of the next generation of plastics.

## 1.2 Metallo-organic Catalysts

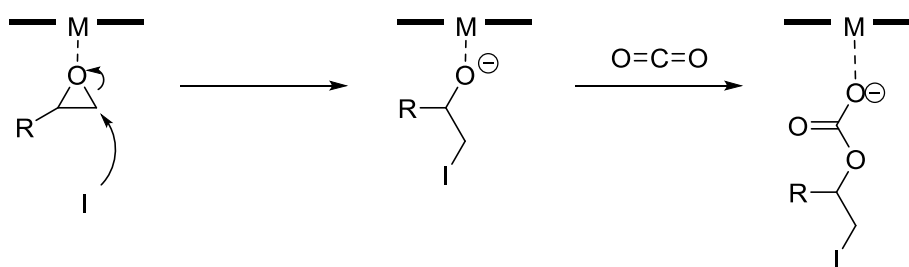
To improve material properties and lower the associated costs of their production, catalyst development has become a primary focus in the synthesis of aliphatic polycarbonates from CO<sub>2</sub> synthons. Metal-based catalysts have garnered the most attention since they often display superior catalytic activities, remain active under mild conditions, and are easily tuneable. Specifically, metals are particularly attractive as catalysts due to their versatile oxidation states and bonding modes (e.g. variability of co-ordination number and the ability to form both  $\sigma$ - and  $\pi$ -bonds).<sup>[30]</sup> Moreover, such catalysts can be easily tuned to modulate activity and/or selectivity via ligand substitution, where the electron density at the metal-center and overall coordination sphere can be altered. As such, both main group and transition metal catalysts have been extensively developed for CO<sub>2</sub>-based polymer synthesis. Before reviewing the updates of metal-based catalysts, the mechanism and kinetics of polycarbonate synthesis will be overviewed.

### 1.2.1 Mechanism and kinetics of copolymerization

#### General mechanism

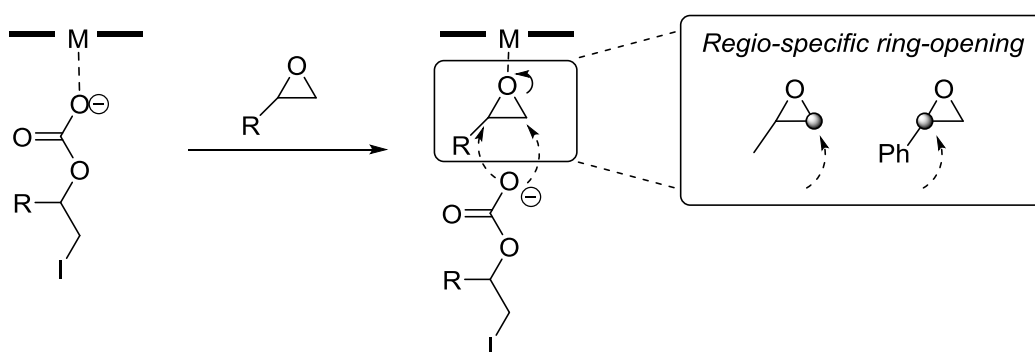
The mechanistic aspects of metal-catalyzed CO<sub>2</sub>/EP copolymerization were first investigated by Tsuruta and co-workers using diethylzinc (ZnEt<sub>2</sub>) as a catalyst where the oxygen-metal (O-M) species (alkoxide) was found to be of prime importance in initiating copolymerization.<sup>[31]</sup> Briefly, direct copolymerization of CO<sub>2</sub>/EP is initiated by a ring-opened epoxide (alkoxide) that can subsequently attack CO<sub>2</sub>, resulting in the formation of carbonate species (Scheme 2).

#### Initiation



**Scheme 2.** The initiation of CO<sub>2</sub>/EP copolymerization.

The ring-opening of the epoxide may *proceed* via different pathways depending on the nature of the terminal group *i.e.* the relative electron donating or electron withdrawing effects of dangling functional groups present on the 3-membered cyclic monomer. For example, the electron-donating methyl group present on the propylene oxide (PO) will favour the epoxide to be opened by methylene ( $-\text{CH}_2-\text{O}-$ ) bond cleavage. Electron withdrawing groups, such as the aromatic phenyl of styrene oxide, on the other hand, will prompt methine ( $-\text{PhCH}-\text{O}-$ ) bond cleavage (Scheme 3).<sup>[32]</sup> It is crucial to note that such cleavages may occur simultaneously during a polymerization process, leading to the production of regio-irregular architectures.<sup>[33]</sup>

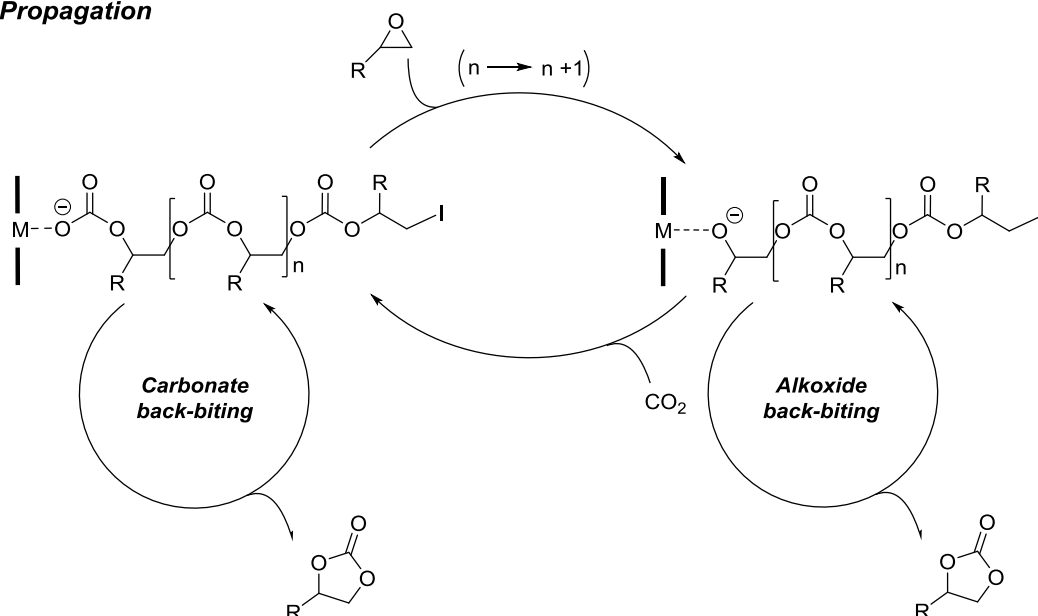


**Scheme 3.** Regio-favoured C–O bond cleavage of epoxide with different substituents.

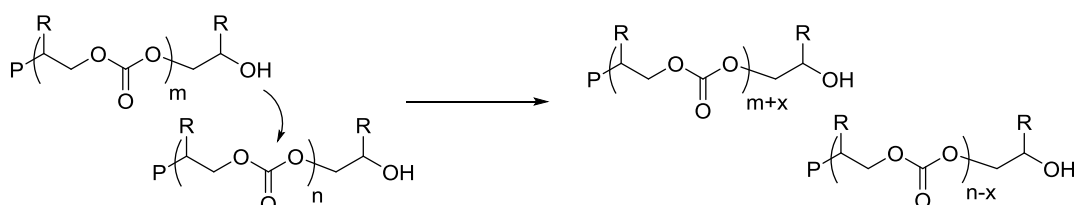
Idealised copolymerization to form polycarbonates involves the cycling between two species (alkoxide and carbonate) from the alternative insertion of epoxide and  $\text{CO}_2$ , while undesirable cyclic by-products or ether domains can be formed and chain-transfer reactions may also occur (Scheme 4).



### Propagation

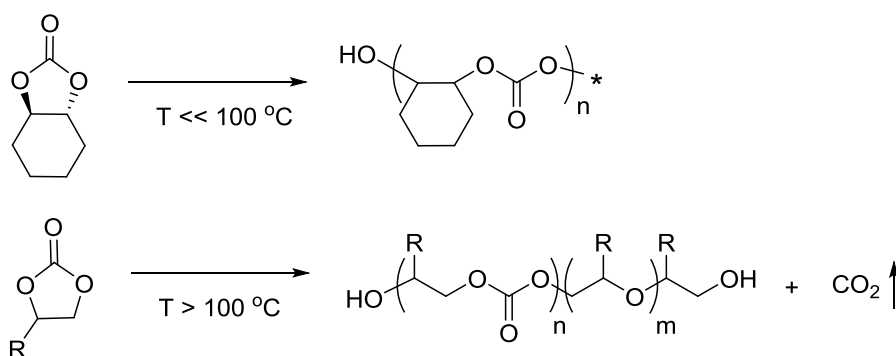


### Chain transfer reaction



**Scheme 4.** The idealised propagation pathway of  $\text{CO}_2/\text{EP}$  copolymerization.

Common by-products in such copolymerizations are five-membered cyclic carbonates (5CCs), which are often produced by back-biting reactions from the activated polymer chain (Scheme 4).<sup>[34]</sup> The formation of 5CCs can be detrimental, since they are thermodynamically stable (apart from *trans*-cyclohexane carbonate (*trans*-CHC) species with a large dihedral angle ( $29.7^\circ$ ,  $-\text{O}-\text{CH}-\text{CH}-\text{O}-$ )<sup>[35]</sup> leading to high ring strain.<sup>[36]</sup> However, 5CCs favour entropically-driven polymerization at high temperatures ( $> 100^\circ\text{C}$ ) resulting in poly(carbonate-co-ether) with the concomitant release of  $\text{CO}_2$  (Scheme 5).<sup>[37]</sup>



**Scheme 5.** Temperature dependent ROP pathways of 5CCs.

### Kinetic perspective

Organometallic-based systems generally yield small amounts of 5CCs, since the activation energy barrier of polymerization ( $E_p$ ) is lower than that of cycle formation ( $E_c$ ) (96.8 vs 137.5 kJ·mol<sup>-1</sup> for  $E_p$  vs  $E_c$ )<sup>[21b]</sup>. The coupling of CO<sub>2</sub>/EP is a first-order process related to the catalyst and epoxide concentration, but has zero-order dependence with respect to the CO<sub>2</sub> pressure.<sup>[38]</sup> However, in Rieger's dinuclear catalytic system, CO<sub>2</sub> pressure dramatically affects the kinetic behaviour of copolymerization. For low pressure conditions (0.5 – 2.5 MPa), the CO<sub>2</sub> insertion is rate limiting, as the reaction displays first-order dependence on CO<sub>2</sub> pressure, and zero-order dependence on epoxide, assuming constant catalyst concentration. From 2.5 – 4 MPa, the reaction becomes zero order with respect to CO<sub>2</sub> and first-order relative to the epoxide. Conversely, under high pressure conditions ( $\geq 5$  MPa), the ring-opening of the epoxide monomer becomes the rate-limiting step.<sup>[38b]</sup>

#### 1.2.2 Main-group metal catalysts

Main group metals, such as Mg, Al and Zn, are attractive alternatives to transition metal-based systems due to their low toxicity and relatively high abundance. Recently, several main group-based homogeneous catalysts that display sufficient activity for CO<sub>2</sub>/EP copolymerizations have been developed.

##### *Mg Catalysts*

Williams and co-workers developed a sophisticated bimetallic complex with macrocyclic ancillary ligands (**Mg-I**, Figure 1) displaying high activity for cyclohexane oxide (CHO) and CO<sub>2</sub> copolymerization to yield poly(cyclohexane carbonate) (PCHC).<sup>[39]</sup> Up to 750 h<sup>-1</sup> TOF was observed, which is 20 times greater than previous Mg-based catalysts<sup>[40]</sup> at 0.01 mol% **Mg-I** catalyst loading (1.2 MPa CO<sub>2</sub> at 100 °C) and without the production of the cyclohexane carbonate (CHC) by-product. The decreased Lewis acidity and the electropositive nature of the magnesium contributes to a strong metal-carbonate bond which enhances the rate of chain propagation compared to cyclic by-product formation. Notably, the high carbonate content in the resulting polymer (> 99%), and near quantitative yields, are even observed in the presence of excess exogenous water. Considering that many organometallic systems (e.g., cobalt-salen complexes) are deactivated in the presence of water,<sup>[41]</sup> this result is particularly important for industrial scale applications, where air- and moisture-free processes can be difficult and costly.

Very recently, a commercially available dialkylmagnesium species (**Mg-II**, Figure 1) effectively catalyzed the isoselective CHO/CO<sub>2</sub> copolymerization (up to 82% isotacticity), which is the first reported use of an achiral catalyst to synthesise a stereo-controlled polycarbonate.<sup>[42]</sup> The TOF was modest at 0.1 MPa (6 h<sup>-1</sup>) and could be increased approximately tenfold (TOF = 62 h<sup>-1</sup> at 1 MPa CO<sub>2</sub>), but at the expense of diminished stereo-control.

### *Al Catalysts*

After a triethylaluminium catalyzed CO<sub>2</sub>/EP copolymerization protocol was reported,<sup>[43]</sup> numerous Al-based catalysts featuring various ligands (such as porphyrin,<sup>[44]</sup> salophen,<sup>[45]</sup> salen,<sup>[46]</sup> and dihydroxy-*p*-tert-butylcalix[4]arene (DMCA)) were explored for polycarbonate synthesis.<sup>[47]</sup> Porphyrin ligands have been ubiquitous in metal complexes for CO<sub>2</sub> copolymerizations because of their well-defined coordination modes and their promotion of reactivity at the axial bond on the metal center, which is perpendicular to porphyrin plane. Bifunctional porphyrin-Al complexes (**Al-I**, Figure 1) have

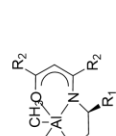
successfully yielded polycarbonates by incorporating CO<sub>2</sub>.<sup>[48]</sup> After installation of electron donating substituents on the porphyrin ligand to modulate the Lewis acidity at the aluminium center, high molecular weight polymers were isolated with decreased cyclic by-products compared to ligands bearing electron withdrawing groups. Before this example, aluminium-porphyrin systems had yielded only low molecular weight polymers ( $M_n = 4.5 \text{ kg}\cdot\text{mol}^{-1}$ ).<sup>[44]</sup> Contrastingly, in another study, aluminium complexes bearing porphyrin ligands substituted with electron withdrawing fragments were more active and afforded polycarbonates with high molecular weights ( $M_n = 33.5 \text{ kg}\cdot\text{mol}^{-1}$ ,  $\bar{D}_M = 1.05$ ).<sup>[49]</sup> Sugimoto and co-workers investigated a series of aluminium chiral catalysts for the enantioselective copolymerization of CO<sub>2</sub> and CHO.<sup>[50]</sup> Al-salen complexes (**AI-II**, Figure 1), activated with tetraethyl acetate (Et<sub>4</sub>NOAc), afforded highly alternating copolymers, but with low molecular weights ( $M_n = 1.9 - 6.8 \text{ kg}\cdot\text{mol}^{-1}$ ,  $\bar{D}_M = 1.14 - 1.22$ ) and modest enantiomeric excesses (ee) up to 23%. Using similar reaction conditions, the selectivity of the reaction was increased by using Al  $\beta$ -ketoiminate complexes (**AI-III**, Figure 1) paired with a Lewis base (N,N-dimethyl-4-aminopyridine) co-catalyst (ee = 49%). The enantioselectivity was further improved to 80% ee by introducing bis-amine Lewis base co-catalysts, however, high molecular weight polymers have still remained elusive. More recently the structurally simple triisobutylaluminium (TiBA) (**AI-IV**, Figure 1) catalyst, coupled with lithium ions as the initiating species, catalyzed the synthesis of alternating polycarbonates in a controlled manner with moderate molecular weights ( $M_n = 19.6 \text{ kg}\cdot\text{mol}^{-1}$ ,  $\bar{D}_M = 1.10$ ).<sup>[51]</sup> Another aluminium-centered catalyst, featuring aminophenolate ligands (**AI-V**, Figure 1), produced moderate molecular weight copolymers from CHO and CO<sub>2</sub> ( $M_n = 29 \text{ kg}\cdot\text{mol}^{-1}$ ,  $\bar{D}_M = 3.16$ ), but only 54% carbonate content was observed in the isolated materials.<sup>[52]</sup> This non-alternating structure, *i.e.* enhanced ether content, is likely the result of the off-target coordination between the aluminium metal center and heteroatoms of the ligand that serve to inhibit the insertion of a carbonate anion.

### *Zn Catalysts*

Although zinc shares characteristics of both main-group and transition metals, the element is better defined as a main-group metal due to the similarities with magnesium such as similar atomic size and preferred oxidation states.<sup>[53]</sup> Since zinc-based catalysts (diethyl zinc/H<sub>2</sub>O) were first screened for the CO<sub>2</sub>/EP copolymerization in 1969, interest in catalyst development has accelerated due to the large relative abundance of the metal.<sup>[31]</sup> A dinuclear zinc structure bearing a macrocyclic ancillary ligand (**Zn-I**, Figure 1) has demonstrated remarkable activity in CO<sub>2</sub>/CHO copolymerization at only 0.1 MPa CO<sub>2</sub>.<sup>[54]</sup> The continued work, using a heterodinuclear (Mg and Zn) system, presents the advantage of being co-catalyst-free, and displays a higher activity compared to with a homodinuclear center.<sup>[55]</sup> The asymmetric  $\beta$ -diketiminato-based Zn catalyst (**Zn-II**, Figure 1) has also displayed good activity in CO<sub>2</sub>/CHO copolymerizations (TOF = 814 h<sup>-1</sup>) when using modest CO<sub>2</sub> pressure (c.a. 1 MPa).<sup>[56]</sup> More recently, Rieger and co-workers developed  $\beta$ -diiminato containing Zn complexes (**Zn-III**, Figure 1), that were very active in the copolymerization of CO<sub>2</sub> with various numerous epoxides, including CHO, propylene oxide (PO), styrene oxide (SO), limonene oxide (LO), octene oxide (OO) and epichlorohydrin (ECH).<sup>[38b, 57]</sup> High catalytic activity (TOF = 5520 h<sup>-1</sup>) was observed at only moderate pressure (4 MPa CO<sub>2</sub>) which is a particularly promising result for potential industrial translation. A reported novel di-zinc catalyst bearing heteroscorpionate ligands (**Zn-IV**, Figure 1) yielded CO<sub>2</sub>/CHO polycarbonates with high molecular weight ( $M_n = 39 \text{ kg}\cdot\text{mol}^{-1}$ ) at 4 MPa CO<sub>2</sub> in just 48 h.<sup>[58]</sup>

Although the CO<sub>2</sub>/CHO copolymerization is often used as a benchmark in academic investigations, the polycarbonates produced from this reaction are not likely to replace commodity plastics because of their inferior thermal and mechanical properties (such as lower  $T_g$ , heat deflection and strength).<sup>[5b, 59]</sup> However, the introduction of a third comonomer to produce terpolymeric architectures provides access to materials with a broader range of thermal and mechanical properties that are positioned to compete with the portfolio of modern thermoplastics (polypropylene or polyethylene for instance). Consequently, interest in terpolymeric structures is increasing and Zn based catalysts have shown particular utility within this area. By combining **Zn-I** complexes in the presence of a yttrium initiator,

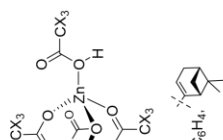
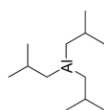
a novel triblock copolymer (poly(lactide)-*b*-poly(cyclohexane carbonate)-*b*-poly(lactide)) was successfully prepared featuring two distinct glass transition temperatures ( $T_{g's} = 60, 80\text{ }^{\circ}\text{C}$ ).<sup>[60]</sup>



u, secBu, Bn, Ph

**I-III**  
 $\text{M}_n = 19.6 \text{ kg} \cdot \text{mol}^{-1}$ ,  $P_M = 1.93$   
 $60^\circ\text{C}$ ,  $1 \text{ MPa CO}_2$   
 Ref [51]

**Al-IV**  
 $\text{CHO/CO}_2$  TOF =  $7 \text{ h}^{-1}$   
 $\text{M}_n = 19.6 \text{ kg} \cdot \text{mol}^{-1}$ ,  $P_M = 1.10$   
 $60^\circ\text{C}$ ,  $1 \text{ MPa CO}_2$   
 Ref [51]



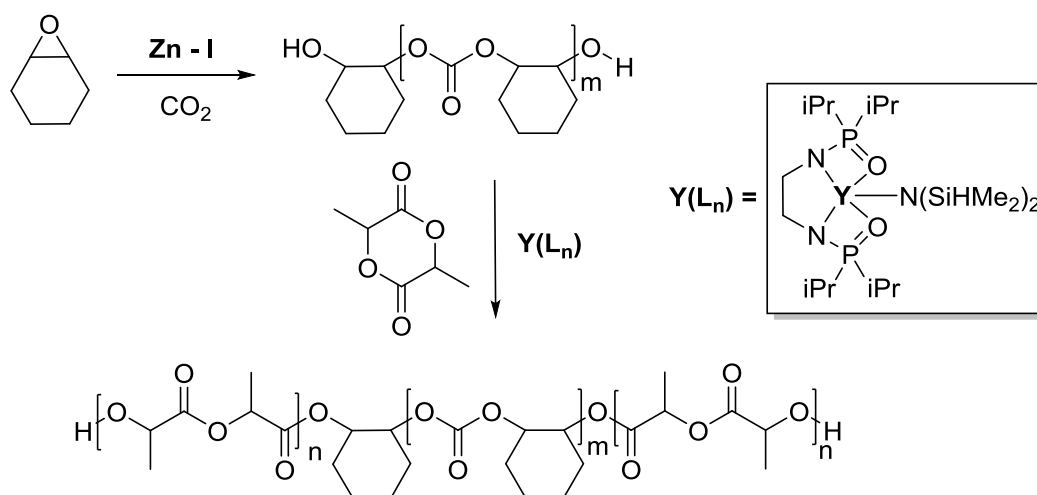
TMS =  $\begin{matrix} \text{CH}_3 \\ | \\ \text{Si} - \text{CH}_3 \\ | \\ \text{H}_3\text{C} \end{matrix}$

**Zn-V**

$\text{B-BU/CHO/CO}_2$   
 $\text{M}_n = 166 \text{ kg} \cdot \text{mol}^{-1}$ ,  $P_M = 1.20$   
 $60^\circ\text{C}$ ,  $4 \text{ MPa CO}_2$   
 Ref [63]

$\text{M}_n = 166 \text{ kg} \cdot \text{mol}^{-1}$ ,  $P_M = 2.10$   
 $60^\circ\text{C}$ ,  $4 \text{ MPa CO}_2$   
 Ref [63]

**Figure 1.** Representative Mg, Al, and Zn-based catalysts for  $\text{CO}_2$ /EP copolymerization.



**Scheme 6.** Copolymerization of CHO and subsequent block copolymerization with lactide.

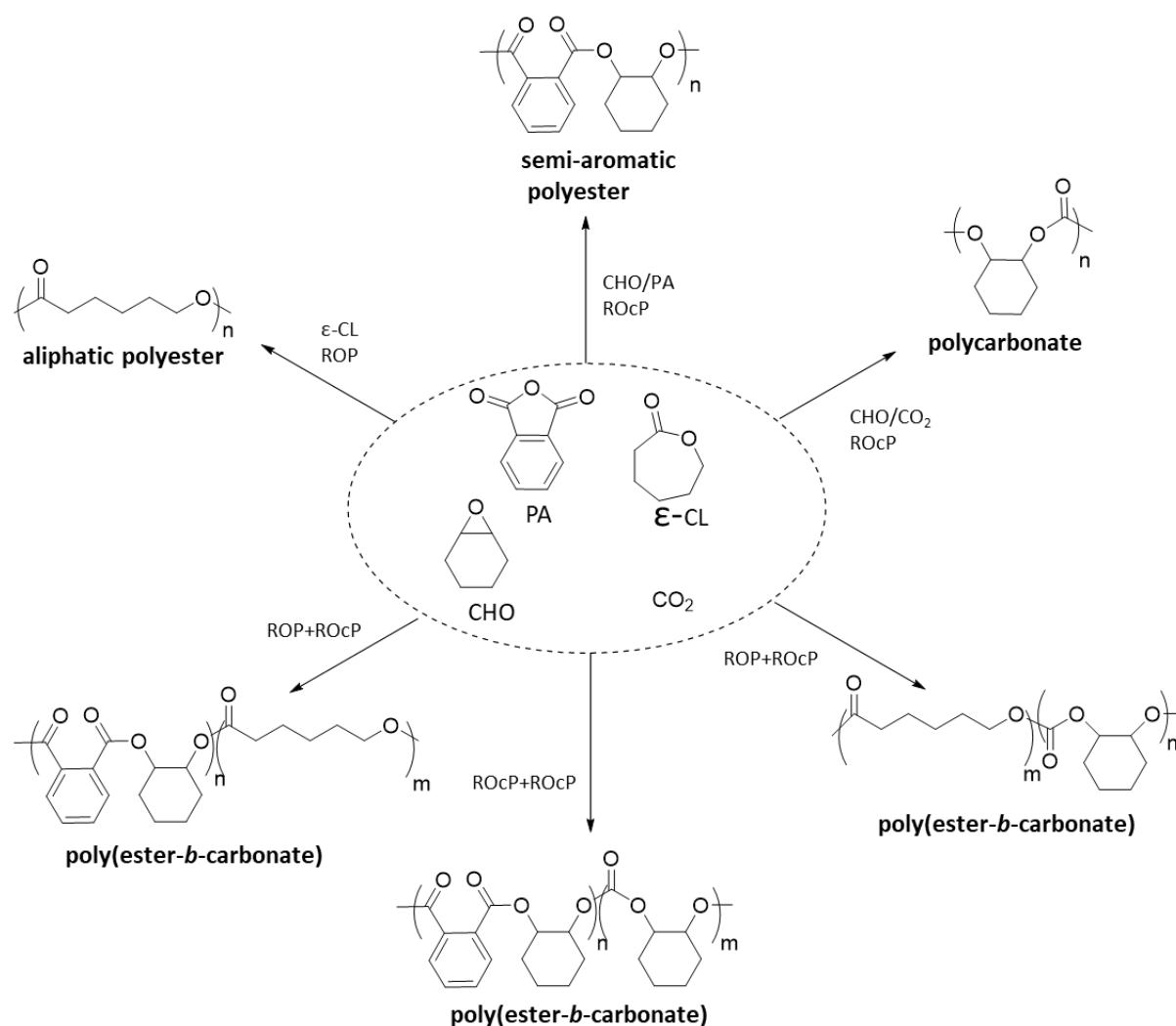
In a similar study, poly( $\epsilon$ -caprolactone)-*b*-poly(cyclohexane carbonate)-*b*-poly( $\epsilon$ -caprolactone) was carried out in one-pot process by combining CHO, CO<sub>2</sub>, and  $\epsilon$ -caprolactone (CL) in the presence of **Zn-I**.<sup>[61]</sup> Rieger reported the **Zn-III** catalysed synthesis of a flexible triblock poly(cyclohexane carbonate)-*b*-poly(dimethylsiloxane)-*b*-poly(cyclohexane carbonate) by using poly(dimethylsiloxane) as a chain transfer agent in order to overcome the inherent brittleness of poly(cyclohexane carbonate).<sup>[62]</sup>

Usually the triblock CO<sub>2</sub>-based polycarbonate synthesis requires a multi-step manipulation and poly-diol as a macro-initiator. This process is both time-consuming and results in fixed sequence of the resultant microstructure which limits the access to more diverse materials and potential corresponding applications. As such, producing block copolymers using simple transformation is promising for the industrial scale utilisation of CO<sub>2</sub>. Thanks to recent advances in catalyst development, simple tuning of the CO<sub>2</sub> pressure to control the sequence of copolymers has become a reality. Moreover, **Zn-V** complexes have been applied to the synthesis of sequence-controlled terpolymers where CO<sub>2</sub> pressure was leveraged as a chemoselective agent in a one-pot synthesis.<sup>[63]</sup>

When subjecting the mixture to low pressure (0.3 MPa CO<sub>2</sub>), a statistical terpolymer ( $M_n = 69 \text{ kg}\cdot\text{mol}^{-1}$ ,  $D_M = 1.60$ ) was furnished from  $\beta$ -butyrolactone ( $\beta$ -BL), CO<sub>2</sub>, and CHO. Using the same monomer combination, a block terpolymer (poly( $\beta$ -BL)-*b*-poly(CHC)) ( $M_n = 146 \text{ kg}\cdot\text{mol}^{-1}$ ,  $D_M = 1.20$ ) was isolated by simply increasing the CO<sub>2</sub> pressure (4 MPa) in the reaction vessel.



Williams and co-workers leveraged **Zn-I** and similar dinuclear catalysts to afford control over polycarbonate microstructures when using a mixed monomer feedstock, where monomer reactivity was dependent upon the nature of the polymer chain-end (Zn-O bond).<sup>[64]</sup> Similarly, Williams and co-workers reported a series of sequence-controlled copolymers from a four-component monomer mixture composed of CL, CHO, phthalic anhydride (PA) and CO<sub>2</sub>. Various copolymeric architectures were obtained in a one-pot methodology, due to the fact that the mechanism can switch between distinct catalytic cycles to effect the microstructure of the growing polymer chain (Figure 2).<sup>[64c]</sup> Some of the unique structures included semi- and full aliphatic polyesters, poly (ester-*b*-ester), polycarbonates, and poly (ester-*b*-carbonate). The ability to rationally tune the polymer microstructure from monomer mixtures is a significant advancement and is particularly applicable for industry applications since it allows access to numerous architectures in a straightforward and potentially more economical manner.



**Figure 2.** A range of polymer products with different microstructures produced using chemo-selective catalysis of a 4-component monomer mixture. <sup>[64c]</sup>

### 1.2.3 Transition metal catalysts

Transition metal catalysis continues to be the cornerstone of many synthetic advances in chemistry because of the high versatility imparted by predictable oxidation-state switching and the facile structural tuning enabled by ligand development and substitution.<sup>[65]</sup> Furthermore, transition metal complexes are generally more resistant to oxidative and/or hydrolytic degradation that can plague many main-group catalyst complexes. However, the glaring weakness is that the natural abundance of some transition metals is extremely low, making them quite expensive and hampering their

sustainability.<sup>[66]</sup> Nevertheless, efforts to improve the recyclability of such catalysts and/or increase catalytic efficiencies should lessen raw material requirements when used in synthetic applications.

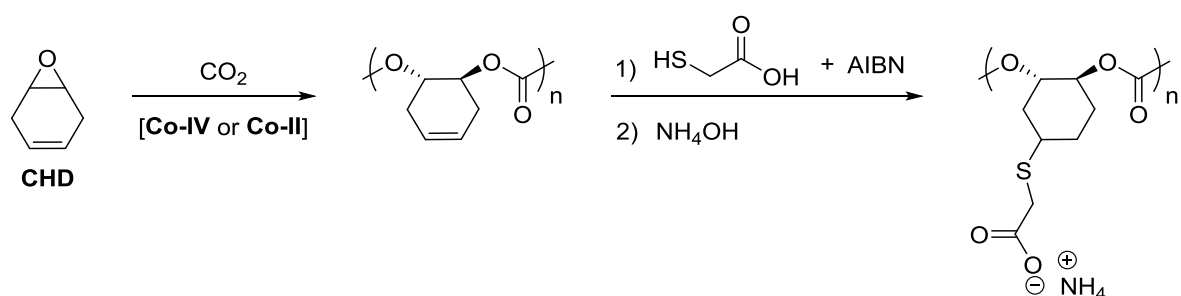
### *Co catalysts*

Organometallic cobalt complexes are some of the best known catalysts that have been particularly effective at catalysing CO<sub>2</sub> copolymerizations, since cobalt has a high Lewis acidity and can adopt a variety of oxidation states.<sup>[41a]</sup> Some of the most studied complexes feature tetradentate – salen ligands<sup>[41c, 67]</sup> and tetraaza macrocycles – porphyrin<sup>[49, 68]</sup> with Co<sup>III</sup> metal centers.

Lu and Darensbourg first reported the preparation of moderate molecular weight ( $M_n = 25.9 \text{ kg}\cdot\text{mol}^{-1}$ ,  $\bar{D}_M = 1.07$ ) alternating CO<sub>2</sub>/epichlorohydrin (ECH) copolymers using Co<sup>III</sup>-based catalysts (Figure 3, **Co-I** and **Co-II**).<sup>[69]</sup> ECH is a notoriously challenging monomer for copolymerization since chloride elimination is a significant competing reaction near ambient temperature (25 °C), contributing to the formation of cyclic carbonate species. Consequently, in the study in question, the activity of the cobalt species was critical with polymerization reaction proceeding below ambient temperatures (0 °C).

The copolymerization of indene oxide (IO) and CO<sub>2</sub> can be conducted under mild reaction conditions using **Co-II** & **Co-III** (Figure 3).<sup>[70]</sup> To obtain high molecular weight polymers, the reaction was performed at 0 °C with low catalyst loading (0.1 mol%), since cyclic carbonate formation is thermodynamically favoured. Although a low catalyst loading (0.1 mol%) led to correspondingly longer induction periods for the binary catalyst system, the resulting polycarbonate was still isolated with reasonable properties ( $M_n = 9.7 \text{ kg}\cdot\text{mol}^{-1}$ ,  $\bar{D}_M = 1.09$ ,  $T_g = 138 \text{ °C}$ ). Using **Co-III** and **Co-IV**, the monomer scope was expanded to include butene oxide (BO), (poly(*trans*-2-butene carbonate),  $M_n = 13.9 \text{ kg}\cdot\text{mol}^{-1}$ ,  $\bar{D}_M = 1.05$ , 24 h)<sup>[71]</sup> and cyclopentane oxide (CPO) (poly(cyclopentane carbonate),  $M_n = 23.5 \text{ kg}\cdot\text{mol}^{-1}$ ,  $\bar{D}_M = 1.06$ , 5 h).<sup>[72]</sup>

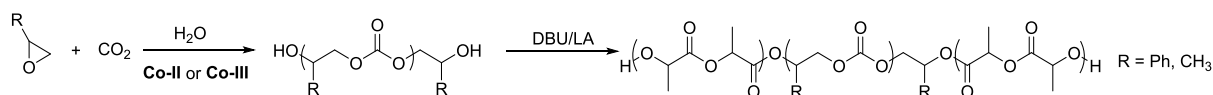
Although polycarbonates with saturated backbones are not very amenable to post-polymerization modifications, the introduction of unsaturated units (e.g. alkenes)<sup>[73]</sup> affords a polymer that can be functionalized via thiol-based click chemistry (Scheme 7).<sup>[74]</sup> The cobalt catalyzed copolymerization of cyclohexadiene oxide (CHDO) and CO<sub>2</sub> affords high molecular weight poly(cyclohexadiene carbonate) ( $M_n = 35.9 \text{ kg}\cdot\text{mol}^{-1}$ ) possessing robust thermal properties ( $T_g = 123 \text{ }^\circ\text{C}$ ), which is slightly higher than the saturated analogue ( $T_g = 116 \text{ }^\circ\text{C}$ ). The replacement of cobalt in **Co-IV** scaffold with other metals such as zinc or magnesium has also been investigated, but the cobalt catalyst displayed superior performance (TOF =  $65 \text{ h}^{-1}$ ) leading to a polymer with higher molecular weight and lower dispersity ( $M_n = 12.9 \text{ kg}\cdot\text{mol}^{-1}$ ,  $D_M = 1.18$ ).<sup>[75]</sup> Regio-chemical considerations have also been investigated in the CHDO/CO<sub>2</sub> system by examining the effect of the alkene in the monomer unit (1,3-CHDO vs 1,4-CHDO).<sup>[76]</sup> Copolymerizations conducted using 1,3-CHDO displayed increased reaction kinetics and yields (40.8% selectivity of polymer formation and 100% conversion for 1,3-CHDO), while inferior catalytic activity was observed for 1,4-CHDO/CO<sub>2</sub> (36.6% selectivity of polymer formation with 57% conversion for 1,4-CHDO), even though poly(1,3-cyclohexadiene carbonate) features a slight lower  $T_g$  (104 – 108 °C) than poly (1,4-cyclohexadiene carbonate) ( $T_g = 123 \text{ }^\circ\text{C}$ ).



**Scheme 7.** Representative functional polycarbonate synthesis (bottom) using cobalt-salen complexes (top) and subsequent post-polymerization functionalization.

Similarly to the zinc catalyzed synthesis of poly(lactide)-*b*-poly(carbonate)-*b*-poly(lactide) materials,<sup>[60]</sup> Co<sup>III</sup> catalysts have also found utility in the preparation of triblock CO<sub>2</sub>-based polymeric structures (Scheme 8). In selected studies, both propylene oxide (PO)<sup>[77]</sup> and styrene oxide (SO)<sup>[78]</sup> were copolymerised with CO<sub>2</sub> to form ABA-type block copolymers with a degradable carbonate-containing

block, respectively. Building upon this concept, more structurally complex co-monomers such as allyl glycidyl ether<sup>[79]</sup> or cyclic phosphates,<sup>[80]</sup> were also successfully copolymerised with CO<sub>2</sub> in the polycarbonate block. These studies highlight a promising route to incorporate CO<sub>2</sub> into more functional materials. Moreover, the advantages imbued by simple one-pot synthesis and increasing monomer diversity should make this method attractive to industry interests.

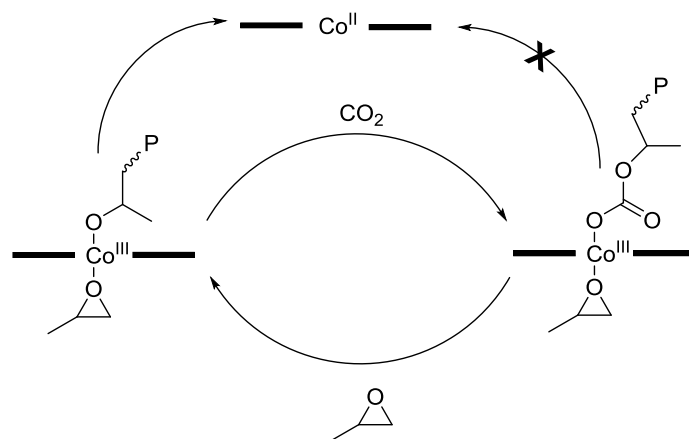


**Scheme 8.** One pot synthesis of poly carbonate-*b*-ester from CO<sub>2</sub>/EP/lactide terpolymerization.

Although mononuclear Co<sup>III</sup>-salen complexes have been widely used for CO<sub>2</sub>/EP copolymerizations, dinuclear systems also demonstrate high activity, yet operate by a distinct mechanism relative to single-site cobalt complexes. In one study, a dinuclear cobalt catalyst with a macrocyclic ancillary ligand yielded a copolymer from CO<sub>2</sub>/CHO under mild conditions (0.1 MPa CO<sub>2</sub>).<sup>[81]</sup> Dissimilar to the alternating insertion of CO<sub>2</sub> and alkoxide in single-site systems, Williams and co-workers proposed a different catalytic cycle for dinuclear catalysts, where the ligated epoxide on one metal center attacks the neighbouring cobalt that is ligated to the carbonate polymer chain-end. Additionally, dinuclear Co<sup>III</sup>-salen species have also been used for stereospecific CO<sub>2</sub>/EP copolymerizations to yield stereocomplexed polycarbonates<sup>[82]</sup> or crystalline gradient terpolymers.<sup>[83]</sup>

As a consequence of their facile synthesis and ease of handling, porphyrin ligands have also been widely investigated in cobalt complexes for CO<sub>2</sub> copolymerizations. Rieger and co-workers demonstrated facile tuning of catalytic activity in single-site metal cobalto-porphyrin complexes, where electron withdrawing substituents on the periphery of the porphyrin led to only cyclic carbonate formation while substitution with electron donating groups (*e.g.* alkoxy group) on the catalyst yielded high molecular CO<sub>2</sub>/PO copolymers ( $M_n = 46.5 \text{ kg}\cdot\text{mol}^{-1}$ ,  $\bar{D}_M = 1.20$ ) at only 30 °C. Following the studies involving single-site cobalt-porphyrin complexes, dinuclear complexes were synthesised and examined in CO<sub>2</sub> copolymerizations.<sup>[84]</sup> In contrast to dinuclear cobalt-salen species,

unfortunately, no rate enhancement or increase in polymer selectivity formation was observed when bis-para-tethered dinuclear complexes were employed for CO<sub>2</sub>/PO copolymerization, suggesting that polymer growth occurs from just a single metal center. For the catalysts featuring a bis-ortho-tethered porphyrin, the polymerization was even more sluggish (likely due to steric constraints) and the cyclic carbonate was the predominant reaction product. As suggested by UV/Vis and NMR experiments, it is likely Co<sup>III</sup>-alkoxide species can hydrolyze to form an inactive Co<sup>II</sup> species.<sup>[84-85]</sup> Nevertheless, polymer formation is still possible if CO<sub>2</sub> insertion occurs and forms the more stable cobalt-carbonate complex (Scheme 9), but this is not as pronounced as in Co<sup>III</sup>-salen complexes.<sup>[35]</sup>



**Scheme 9.** The possible propagation route and deactivation pathways for Co<sup>III</sup> catalyzed CO<sub>2</sub>/PO polymerizations (where P represents the growing polymer chain).<sup>[86]</sup>

### Cr catalysts

Chromium-salen complexes generally perform markedly worse than their cobalt analogues often leading to lower amounts of polymer formation due to diminished catalytic activities.<sup>[70-73, 87]</sup> Likewise, this observation is also apparent for thio-ligated chromium catalysts.<sup>[88]</sup> It has been hypothesised that the inferior nature of chromium species is a consequence of the larger spherical volume of six-coordinate Cr (relative to Co) that promotes back-biting along the polymer chain.<sup>[89]</sup> To overcome this issue, a chromium catalyst featuring a less sterically hindered salen-type ligand (**Cr-I**) was investigated in the copolymerization of 1,4-dihydronaphthalene oxide (DNO) and CO<sub>2</sub> (Figure 3).<sup>[90]</sup>

The planar geometry of the azaannulene ligand opened up the coordination sphere around the metal center and allowed the polymerization to proceed to 63% conversion with only 11% cyclic carbonate formation ( $\text{TOF} = 23 \text{ h}^{-1}$ ). However, a chromium complex bearing the classic salen ligand (tert-butyl substituents) (**Cr-II**) resulted in poor conversion (32%) and larger amounts of cyclic carbonate by-product (39%) with a modest TOF ( $11 \text{ h}^{-1}$ ).

Kozak developed a series of  $\text{Cr}^{\text{III}}$  amino-bis(phenolato) (ABP) catalysts (**Cr-III**, Figure 3) for  $\text{CO}_2/\text{CHO}$  copolymerizations to yield moderate molecular weight polycarbonate ( $M_n = 13.1 \text{ kg}\cdot\text{mol}^{-1}$ ,  $\bar{D}_M = 1.40$ ) in just 24 h at low catalyst loading (0.2 mol% Cr and 0.1 mol% co-catalyst).<sup>[91]</sup> Both *trans* and *cis* geometries feature an accessible, vacant coordination site allowing an ionic species to coordinate with the metal center. Although the chloride-bridged dimer was isolated and confirmed by X-ray diffraction, it is likely that the monometallic five-coordinate complex that is ligated by ionic cocatalysts (e.g. azide, chloride) is involved in the catalytic cycle, since the combination of the co-catalyst and  $\text{Cr}^{\text{III}}$  dimer affords a heterogeneous mixture in neat CHO. **Cr-III** with co-catalysts are also active in the copolymerization of  $\text{CO}_2$  with PO with decent activity ( $\text{TOF} = 48 \text{ h}^{-1}$ ) at a mild temperature ( $25^\circ\text{C}$ ).<sup>[92]</sup>

In a follow-up study in 2014, two similar chromium complexes featuring either a tridentate and tetradentate ligand were synthesised by replacing the pyridyl arm of **Cr-III** with either a non-coordinating benzyl moiety (**Cr-IV**, Figure 3) or a tetrahydrofuranyl group of modest donicity (**Cr-V**, Figure 3).<sup>[93]</sup> Overall, the tridentate complex resulted in lower molecular weight polymers ( $M_n = 3.8 \text{ kg}\cdot\text{mol}^{-1}$ ,  $\bar{D}_M = 1.48$ ), likely due to catalyst instability, while the tetradentate ligand led to better results ( $M_n = 6.4 \text{ kg}\cdot\text{mol}^{-1}$ ,  $\bar{D}_M = 1.42$ ). Notably, **Cr-V** still performed worse than **Cr-III**, likely due to the weaker donating ability of the ethereal oxygen in the tethering group, thus highlighting the critical importance of ligand tuning. A recent work from Kozak and co-workers described a new complex where the tetrahydrofuranyl moiety in **Cr-IV** was replaced with the more strongly donating amino

group (**Cr-VI**, Figure 3), which led to an improvement of the CO<sub>2</sub>/CHO copolymerization providing a controlled, high molecular weight polycarbonate ( $M_n = 35 \text{ kg}\cdot\text{mol}^{-1}$ ,  $D_M = 1.12$ ).<sup>[94]</sup>

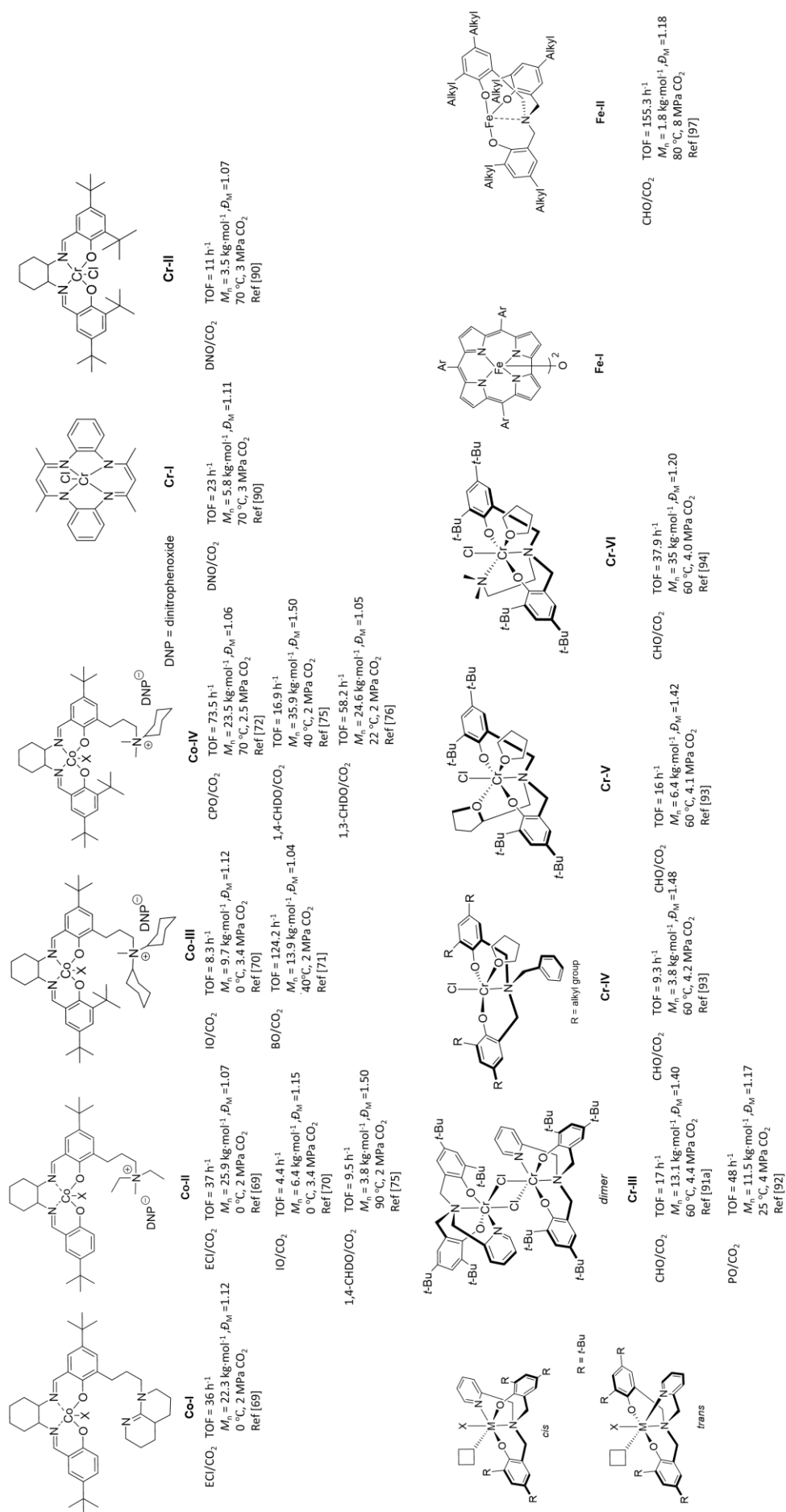
Cr-porphyrin complexes have also been screened in the synthesis of CO<sub>2</sub>-based polycarbonates.<sup>[68f, 95]</sup> When compared to main-group containing Al-porphyrin counterparts<sup>[48b]</sup>, the catalytic activity of chromium complexes are less dependent on CO<sub>2</sub> pressure, since CO<sub>2</sub> insertion is more favourable due to the high oxidation state (III) of the chromium in the organometallic complex (3 MPa CO<sub>2</sub> for Al-porphyrin vs 0.1 MPa for CO<sub>2</sub> Cr-porphyrin).<sup>[68f]</sup> Furthermore, porphyrin containing chromium catalysts generally display better kinetics (TOF = 150 h<sup>-1</sup>) than structurally similar aluminium (TOF = 73 h<sup>-1</sup>) or cobalt (TOF = 140 h<sup>-1</sup>) analogues. This is probably due to the higher polarity, and thus reactivity, of the M-O bond in the chromium catalysts.<sup>[68d]</sup>

### *Fe catalysts*

Since iron is one of the most Earth-abundant metals, there are considerable financial and environmental motivations to develop catalytic systems with comparable activity to the robust transition metal-based catalysts. Nozaki reported the copolymerization of various epoxides with CO<sub>2</sub>, such as PO, CHO, and glycidyl phenyl ether (GPE), using Fe-corrole catalysts (**Fe-I**, Figure 3).<sup>[96]</sup> However, the incorporation of CO<sub>2</sub> was minimal (9%) at 60 °C (2 MPa CO<sub>2</sub>, 1 h), affording primarily a polyether. Another Fe-based catalyst (**Fe-II**, Figure 3) displayed switchable polymerization behaviour (selectivity for cyclic vs linear topology).<sup>[97]</sup> By increasing the ratio of co-catalyst (tetrabutylammonium halide, Bu<sub>4</sub>NX, X = Cl, Br or I), the cyclic polymer was isolated, as the nucleophile rapidly replaced the M-OCO<sub>2</sub> adduct to inhibit propagation. In contrast, low catalyst loading of both Fe-complexes and corresponding halide (**Fe-II**: Bu<sub>4</sub>NCl = 1:1, 0.5 mol%) promoted the formation of a linear structure, even when supercritical CO<sub>2</sub> (8 MPa) was employed as the reaction medium at 85 °C for 3 h.



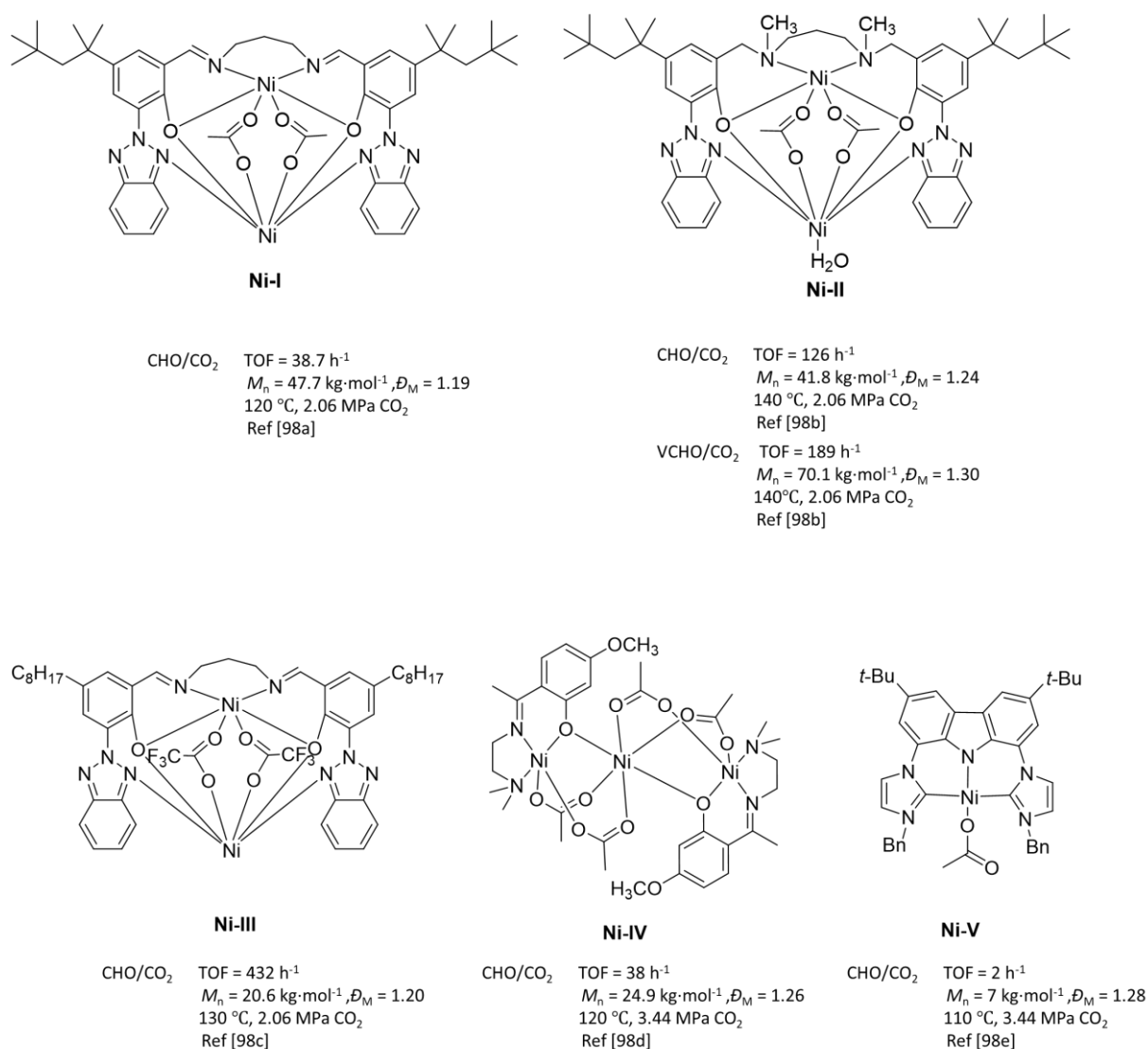




**Figure 3.** Representative Co, Cr, and Fe-based catalysts for CO<sub>2</sub>/EP copolymerization.

## *Ni catalysts*

Ko and co-workers have largely pioneered nickel-catalyzed CO<sub>2</sub>/EP copolymerizations.<sup>[98]</sup> The imine-chelated complex (**Ni-I**, Figure 4), in particular, proved remarkably active (in the absence of a co-catalyst) in the ROCOP of CO<sub>2</sub>/CHO (TON = 2484, TOF = 38.7 h<sup>-1</sup>,  $M_n$  = 47.7 kg·mol<sup>-1</sup>,  $D_M$  = 1.19).<sup>[98a]</sup> By modifying the bonding environment of the nitrogen atoms (imine to amine), the resulting nickel catalyst (**Ni-II**, Figure 4) displayed increased stability and efficiency (TON > 4000) under similar reaction conditions.<sup>[98b]</sup> The same catalyst (**Ni-II**) also performed well when the alkene containing monomer 4-vinyl-1,2-cyclohexane oxide (VCHO) was used, thus showing the potential to create a functional polycarbonate. Following this study, the acetate bridge in **Ni-I** was substituted with a trifluoroacetate linker (**Ni-III**, Figure 4) and higher efficiency was observed (TON = 1728, TOF = 432 h<sup>-1</sup>).<sup>[98c]</sup> Other modified Ni-based catalysts with Schiff base ligands (**Ni-IV**, Figure 4)<sup>[98d]</sup> or carbene ligands (**Ni-V**, Figure 4)<sup>[98e]</sup> have also displayed some catalytic activity in CHO/CO<sub>2</sub> copolymerizations (**Ni-IV**, TON = 840 and **Ni-V**, TON = 280), but these metrics are relatively low compared to the salen-type Ni complexes (see **Ni-I**, **Ni-II** and **Ni-III**).

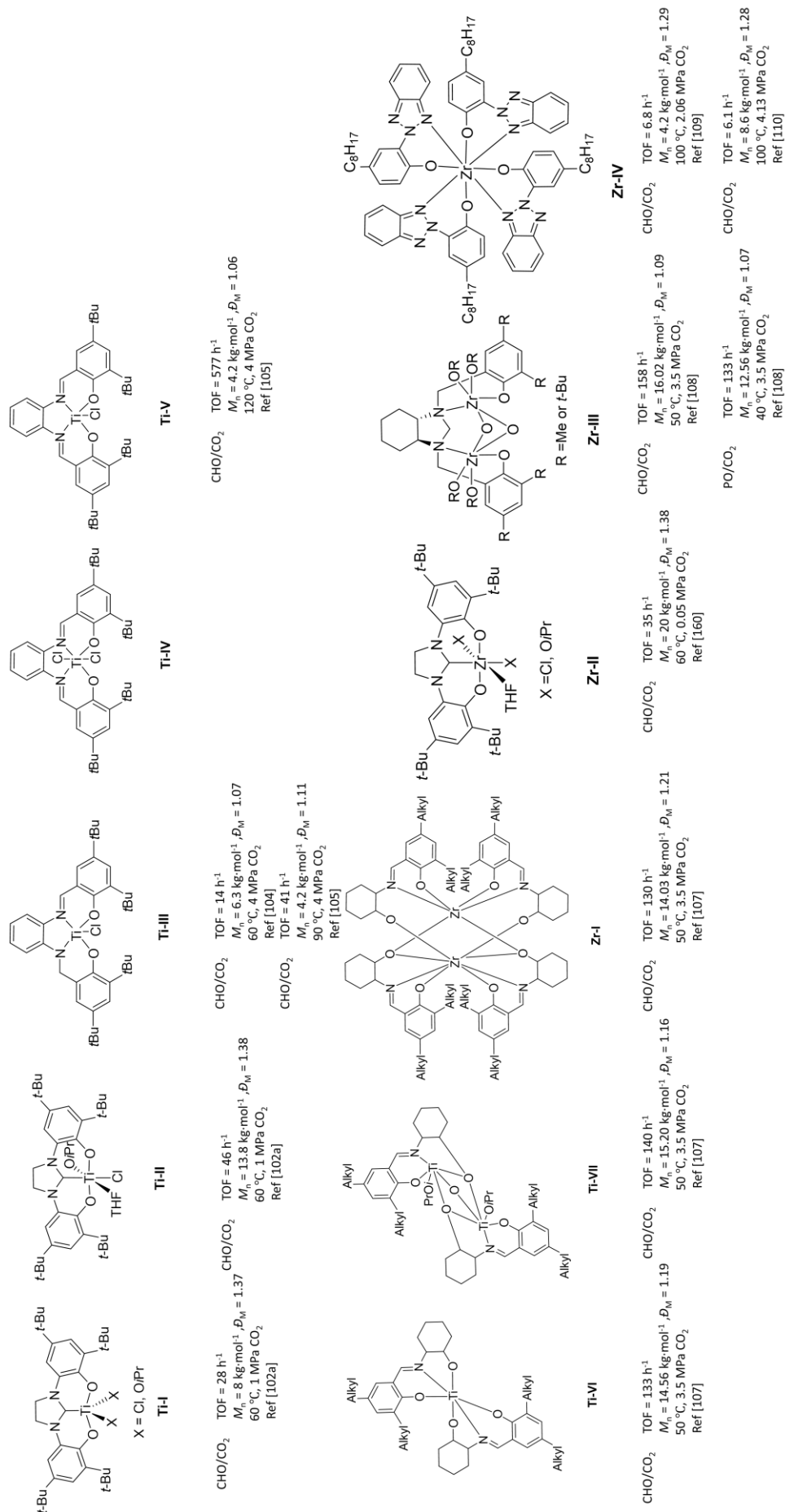


**Figure 4.** Representative Ni-based complexes for CO<sub>2</sub>/EP copolymerization.

### Ti, Zr, Hf Catalysts

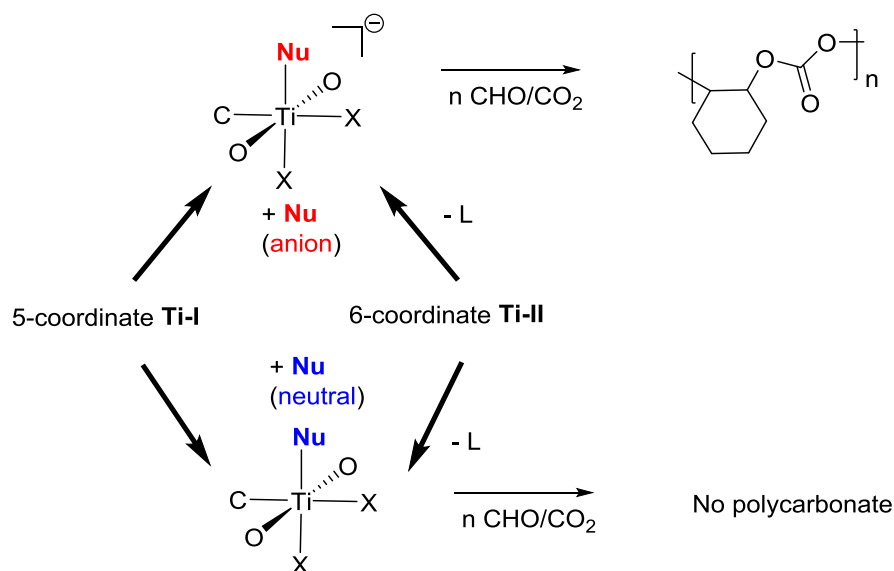
Group IV transition metal complexes (Ti, Zr, and Hf) have only recently been explored in CO<sub>2</sub>-based copolymerization reactions, but they have proven remarkably effective thus far. The first instance of tetravalent group IV catalyzed copolymerization of CO<sub>2</sub>/PO was reported in 2011.<sup>[99]</sup> *N*-heterocyclic carbenes (NHC) bear a lone electron pair which can serve as a ligand, in which the ease of dissociation from the metal center, in part, determines the reactivity of the metal centre.<sup>[100]</sup> Such dissociation can be overcome by the introduction of anionic tether moieties to NHC.<sup>[101]</sup> Ti catalysts bearing a bis-anionic NHC pincer ligand (**Ti-I**, Figure 5) or (**Ti-II**, Figure 5) were investigated in CO<sub>2</sub>-

based copolymerizations and in the absence of an activating halide co-catalyst only the polyether was observed.<sup>[102]</sup>



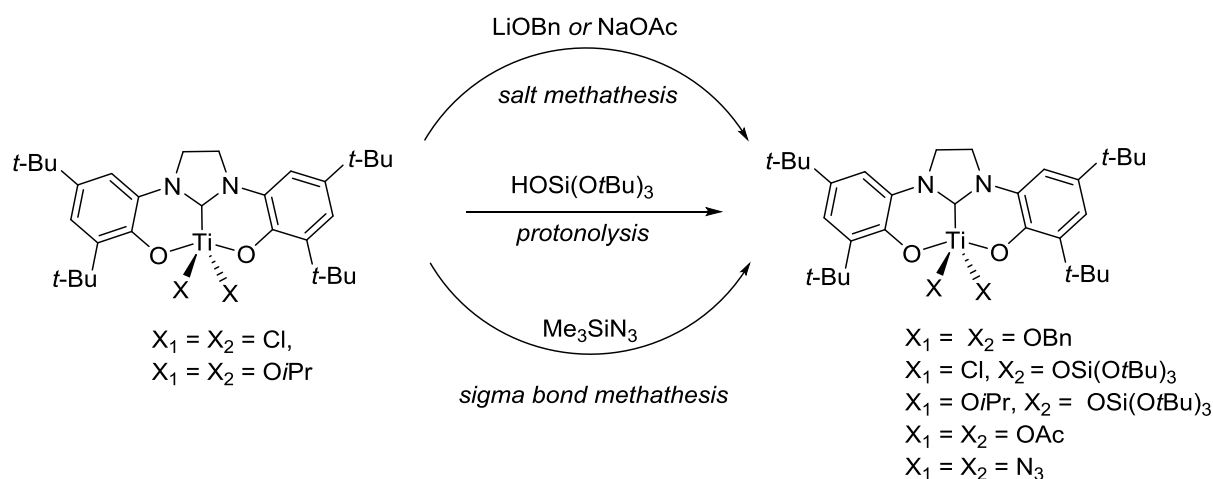
**Figure 5.** Representative Ti and Zr-based catalysts for CO<sub>2</sub>/EP copolymerization.

Le Roux postulated that six-coordinate titanium complex served as a crucial intermediate species in the mechanism of polycarbonate formation after undergoing anion exchange (Cl or O<sup>i</sup>Pr from the co-catalyst) since the addition of neutral co-catalysts, like DMAP, did not promote polycarbonate formation (Scheme 9).<sup>146</sup>



**Scheme 9.** The proposed mechanism of Ti-catalyzed CO<sub>2</sub>/CHO copolymerization.

The catalytic system was further improved by substituting the halide co-catalyst for larger anions, including benzyl oxide (OBn), acetate (OAc), azide (N<sub>3</sub>) and tri-tert-butyl silicate oxide (OSi(OtBu)<sub>3</sub>) (Figure 6).<sup>[103]</sup> In the presence of relatively bulky organic salts, such as bis(triphenylphosphine)iminium (PPN) chloride or azide (PPNCl or PPNN<sub>3</sub>), the copolymerization CHO and CO<sub>2</sub> was active under extremely low CO<sub>2</sub> pressure (0.05 MPa) to afford a polycarbonate ( $M_n = 7.7$  kg·mol<sup>-1</sup>,  $\mathcal{D}_M = 1.54$ ) within 15 minutes. However, the overall conversion remained low (< 35%), even after a prolonged reaction time.



**Figure 6.** Synthetic route of Ti-based catalysts with various anions.

The scope of salen-based catalysts was expanded by introducing titanium as the active metal center (**Ti-III**, Figure 5).<sup>[104]</sup> However, when applied in a  $\text{CO}_2/\text{CHO}$  copolymerization, only modest molecular weight polycarbonate was isolated ( $M_n$  up to  $6.3 \text{ kg}\cdot\text{mol}^{-1}$ ) at 4 MPa  $\text{CO}_2$  and 60 °C after 20 h. Moreover, the coordinatively saturated Ti-salen complex (**Ti-IV**, Figure 5) only afforded cyclic carbonate, even in the presence of the large PPNCI co-catalyst. This confirmed the conclusion of Erwan and co-workers, who had also implicated this nucleophile exchange from co-catalysts as a crucial step before chain propagation.<sup>[102a]</sup> They also observed that employing a di-anionic ligand (**Ti-V**, Figure 5) increased the catalytic activity ( $\text{TOF} = 577 \text{ h}^{-1}$  for 1 h) relative to a catalyst bearing a tri-anionic ligand (**Ti-III**) ( $\text{TOF} = 41 \text{ h}^{-1}$  for 8 h).<sup>[105]</sup>

A heterodinuclear Ti/Zn catalyst was recently synthesized and screened in  $\text{CO}_2/\text{EP}$  copolymerizations, however, only low molecular weight polycarbonates were produced ( $M_n = 2 \text{ kg}\cdot\text{mol}^{-1}$ ,  $\bar{D}_M = 1.35$ ).<sup>[106]</sup> It is possible that this poor activity is due to the minimally active polymer chain exchange between the Ti and Zn center, similar to the dinuclear mechanism proposed for dinuclear zinc catalysts.<sup>[106]</sup> Nevertheless, other complexes that feature half salen ligands paired with Ti, Ti-Ti or Zr-Zr metal centers (**Ti-VI**, **Ti-VII** or **Zr-I**, Figure 5) have exhibited great activity and control (for example, yielding poly(CHC) with  $M_n = 15.2 \text{ kg}\cdot\text{mol}^{-1}$  and 84% carbonate content) for a wide substrate scope (including LA,  $\epsilon\text{-CL}$ , CHO, PO and SO).<sup>[107]</sup>

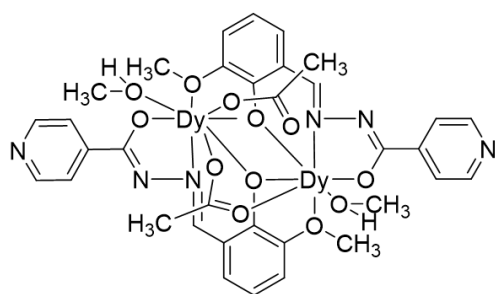


Le Roux and co-workers recently reported Zr-NHC complexes (**Zr-II**, Figure 5) for the synthesis of poly(CHC).<sup>[108]</sup> Unlike the sluggish performance of the Ti-NHC/DMAP catalytic system, the Zr-NHC/DMAP mixture was more active, potentially due to the larger coordination sphere of zirconium, where both anion and neutral co-ligands could be accommodated to form a stable six-coordinate species. A Zr-salen catalyst (**Zr-III**, Figure 5) was also active in different polymerization pathways, including the ROP of LA,  $\epsilon$ -CL and epoxide, or the ROCOP of CO<sub>2</sub>/EP where moderate molecular weight polycarbonates ( $M_n = 16.02 \text{ kg}\cdot\text{mol}^{-1}$ ,  $D_M = 1.09$ ) were obtained under relatively mild reaction conditions (50 °C, 3.5 MPa CO<sub>2</sub>).<sup>[109]</sup>

The benzotriazole phenolate (bis-BZH) chelating species was used to form various group IV (Ti, Zr, Hf) complexes possessing ethereal bridges.<sup>[110]</sup> The catalysts were assessed for activity in both ROP of LA and ROCOP of CO<sub>2</sub>/CHO, and Zr-bis-BZH complexes displayed decent performance (TOF = 6.8 h<sup>-1</sup>) for CO<sub>2</sub>-based polycarbonate synthesis compared to Hf analogues (TOF = 3 h<sup>-1</sup>). Tetra-benzotriazole phenolate(BZH) group IV complexes were also investigated in CO<sub>2</sub>/CHO copolymerizations with the Zr- catalyst (**Zr-IV**) again outperforming group IV analogues to afford a controlled ( $D_M = 1.28$ ) polycarbonate with moderate molecular weight (**Zr-IV**  $M_n = 8.6 \text{ kg}\cdot\text{mol}^{-1}$ , 93 % carbonate content vs Hf-BZH  $M_n = 4 \text{ kg}\cdot\text{mol}^{-1}$  76 % carbonate content vs Ti-BZH,  $M_n = 0 \text{ kg}\cdot\text{mol}^{-1}$ ). The order of reactivity for the complexes follows Zr ~ Hf > Ti, possibly explained by the larger atomic radii of Zr and Hf that may open up the coordination sphere relative to the smaller Ti metal center.<sup>[111]</sup>

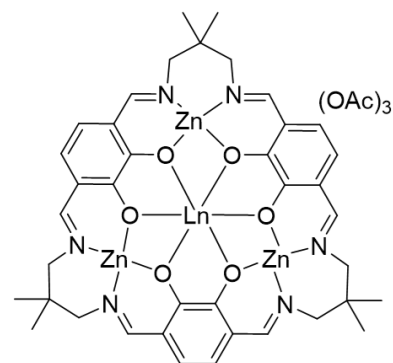
### *Lanthanide Catalysts*

Compared to the large number of investigations involving transition metal complexes, lanthanide catalysts have been largely ignored. Nevertheless, some lanthanide complexes can possess superior air-stability relative to transition metal species, and this should provide a great advantage in CO<sub>2</sub> copolymerization processes. Dysprosium Schiff-base complexes (**Dy-I**, Figure 7) were observed to be robust catalysts for CO<sub>2</sub>/CHO copolymerization (TON = 1620), yielding moderate molecular weight polycarbonate (up to  $M_n = 22 \text{ kg}\cdot\text{mol}^{-1}$ ) under optimised conditions (3.44 MPa CO<sub>2</sub>, 100 °C). However, in this case, the dispersities of the polymers ( $\mathcal{D}_M = 2.02 - 5.69$ ) were quite high, indicating significant termination or chain-transfer processes.<sup>[112]</sup>



**Dy-I**

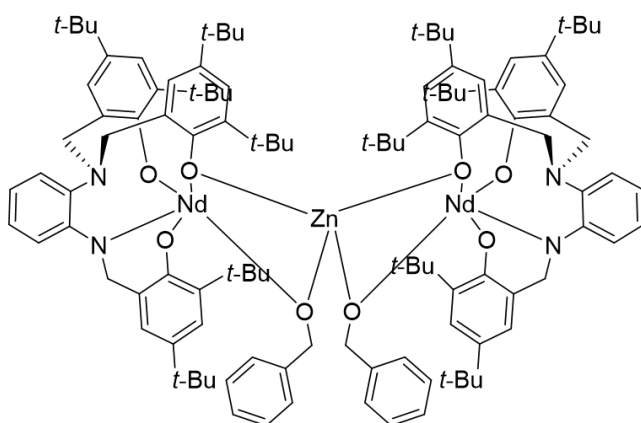
CHO/CO<sub>2</sub> TOF = 17 h<sup>-1</sup>  
 $M_n = 22 \text{ kg} \cdot \text{mol}^{-1}$ ,  $\mathcal{D}_M = 5.12$   
 100 °C, 3.44 MPa CO<sub>2</sub>  
 Ref [164]



Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Dy

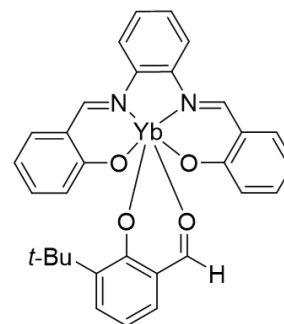
**La-I**

CHO/CO<sub>2</sub> TOF = 370 h<sup>-1</sup>  
 $M_n = 14 \text{ kg} \cdot \text{mol}^{-1}$ ,  $\mathcal{D}_M = 1.30$   
 100 °C, 0.6 MPa CO<sub>2</sub>  
 Ref [165]



**Nd-I**

CHO/CO<sub>2</sub> TOF = 82 h<sup>-1</sup>  
 $M_n = 295.8 \text{ kg} \cdot \text{mol}^{-1}$ ,  $\mathcal{D}_M = 1.65$   
 25 °C, 0.7 MPa CO<sub>2</sub>  
 Ref [166]



**Yb-I**

CHO/CO<sub>2</sub> TOF = 12 h<sup>-1</sup>  
 $M_n = 11.4 \text{ kg} \cdot \text{mol}^{-1}$ ,  $\mathcal{D}_M = 1.35$   
 70 °C, 2 MPa CO<sub>2</sub>  
 Ref [167]

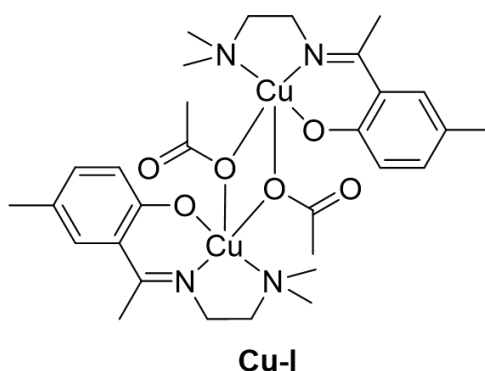
**Figure 7.** Representative lanthanide-based catalysts for CO<sub>2</sub>/EP copolymerization.

Inspired by the salen dinuclear complexes from Williams' group,<sup>85</sup> mixed heterometallic structures, featuring a lanthanide (Ln) and main group metal (Zn) connected via a macrocyclic tri(salen) ligand (**La-I**, Figure 7), were found to possess the unique property of rapid inter-/intra-molecular acetate ligand exchange.<sup>[113]</sup> After careful screening of several lanthanide metals, the Ce/Zn complex exhibited superior catalytic performance (TOF = 370 h<sup>-1</sup>). Telomerisation of CO<sub>2</sub>/CHO copolymerization was successful by adjusting the amount of acetate counterion, resulting in a

polymer with “controllable” molecular weight. The heterometallic (Nd/Zn) complex (**Nd-I**, Figure 7) afforded extremely high molecular weight polycarbonates ( $M_n = 295 \text{ kg}\cdot\text{mol}^{-1}$ ,  $\bar{D}_M = 1.65$ ) in just 12 h under mild conditions (25 °C, 0.7 MPa CO<sub>2</sub>).<sup>[114]</sup> Moreover, the polymer molecular weight was found to be extremely sensitive to the reaction temperature, for example  $M_n \sim 50 \text{ kg}\cdot\text{mol}^{-1}$  at 70 °C and this inverse relationship continued at higher temperatures. It was surmised that at elevated temperatures the catalyst could also degrade the polymer backbone since there is an equilibrium between propagation and depolymerization, which favours the latter as the temperature increases. A ytterbium-salen complex (**Yb-I**, Figure 7) paired with halide co-catalysts was found to be quite active for CO<sub>2</sub>/CHO copolymerizations with optimised conditions furnishing a polycarbonate with  $M_n = 11.4 \text{ kg}\cdot\text{mol}^{-1}$  at 2 MPa CO<sub>2</sub> and 70 °C.<sup>[115]</sup> Other lanthanides (Sc, Y) were also examined in the same organometallic framework, but they displayed diminished activity.

### Cu Catalysts

Although Cu organometallic complexes have been widely studied in both small molecule and polymerization catalysis (for example controlled radical polymerization), they are relatively unexplored as CO<sub>2</sub>/EP copolymerization catalysts. In fact, there is only one such study as reported by Ko and co-workers (**Cu-I**, Figure 8) which demonstrated unremarkable activity (TOF = 11.5 – 18.8 h<sup>-1</sup>).<sup>[116]</sup>



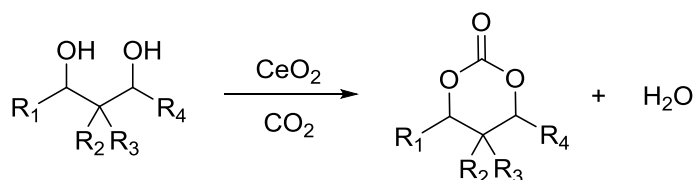
CHO/CO<sub>2</sub>    TOF = 18.8 h<sup>-1</sup>  
 $M_n = 3.4 \text{ kg}\cdot\text{mol}^{-1}$ ,  $\bar{D}_M = 1.31$   
 120 °C, 2.06 MPa CO<sub>2</sub>  
 Ref [116]

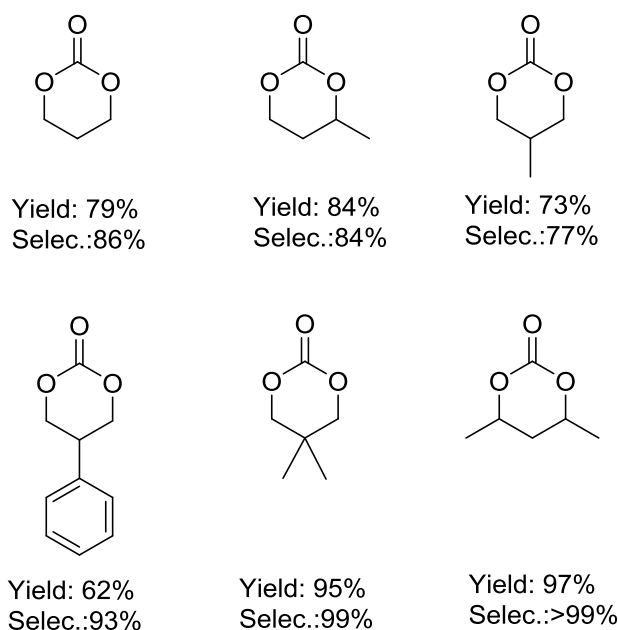
**Figure 8.** Representative Cu-based catalysts for CO<sub>2</sub>/EP copolymerization.

#### 1.2.4 Novel Cyclic Carbonate Monomers derived from CO<sub>2</sub>

Although direct incorporation of CO<sub>2</sub> into macromolecular architectures using copolymerization strategies represents a convenient path to more sustainable polymers, an alternative method for incorporating CO<sub>2</sub> into polymers is to use it as a reagent in the synthesis of cyclic carbonate monomers from naturally-derived alcohols. Initially, five-membered cyclic carbonates (5CC) were investigated as precursors to polycarbonates, however, ring opening is unfavourable without the elimination of CO<sub>2</sub>. As such, attention has turned to six-membered cyclic carbonates (6CC) that can undergo controlled ROP using either metal- or organo- catalysts.<sup>[117]</sup> This strategy does not simply increase the valorisation of CO<sub>2</sub>, but broadens the functional group scope of the resulting polycarbonates, potentially leading to new materials with interesting thermal and/or mechanical properties.

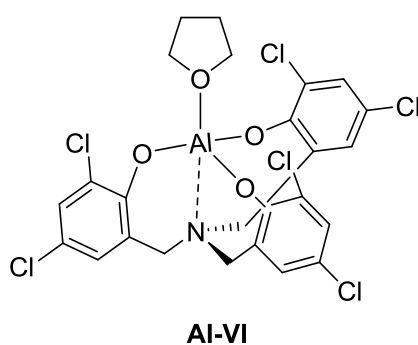
One of the most common established routes to 6CCs is the cerium (IV) oxide (CeO<sub>2</sub>) catalyzed coupling of CO<sub>2</sub> and various diols (Figure 9).<sup>[10a, 10b]</sup>





**Figure 9.** (a) Synthesis of six-membered cyclic carbonates from the corresponding diol substrates. (b) The library of six-membered cyclic carbonates synthesized from CO<sub>2</sub> and various diols. <sup>[10a]</sup>

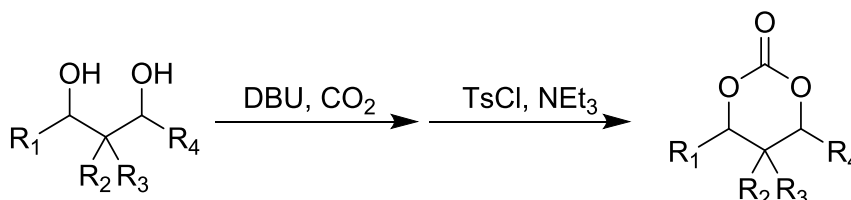
After the pioneering trimethylene carbonate (TMC) synthesis using oxetane and CO<sub>2</sub> by Baba<sup>[29, 118]</sup> and Darensbourg<sup>[119]</sup>, Kleij's group developed an aluminium-catalyzed coupling reaction between a heterocyclic oxide and CO<sub>2</sub> (**AI-VI**, Figure 10).<sup>[22b]</sup> The reaction method is particularly effective for the synthesis of functional 5CCs and TMC. However, the analogous coupling reaction for producing a 6CC using CO<sub>2</sub> and 3,3-dimethyloxetane is not very selective (54%) and is low yielding for 6CC product formation (26% yield), presumably due to steric inhibition from the adjacent methyl groups.



**Figure 10.** Representative aluminium catalyst for 6CC synthesis.

### 1.3 Organocatalysts

In an effort to address environmental concerns including impacts to health, high cost and the inherent oxygen and moisture lability of metal-based catalysts, metal-free methods for CO<sub>2</sub>-based polycarbonate synthesis have been developed contemporaneously. Although organocatalysts present essential green chemistry benefits, they have traditionally lagged behind their metal counterparts in terms of stability and activity. Nevertheless, the development of robust organocatalysts for polycarbonate synthesis remains a priority. Organocatalysts have been successfully employed to activate CO<sub>2</sub> for the synthesis of cyclic carbonate monomers, such as 5CCs,<sup>[120]</sup> but these monomers are not particularly suitable for ring-opening protocols. Furthermore, efforts aimed at incorporating CO<sub>2</sub> into copolymeric structures while suppressing the formation of 5CC products have traditionally yielded predominantly cyclic by-products instead (Scheme 3). As previously mentioned, the synthesis of 6CCs (from CO<sub>2</sub> and oxetane substrates mentioned in section 1.2.4), is an alternative approach to using CO<sub>2</sub> in polycarbonate synthesis. However, the dramatic difference of acidity between epoxide and oxetane has made organocatalyzed approaches more challenging.<sup>[23c, 23d]</sup> Nevertheless, Buchard and co-workers reported the first instance of 6CCs synthesised from corresponding diols and CO<sub>2</sub> at very low pressure (0.1 MPa CO<sub>2</sub>) (Scheme 10) using 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) in 2015.<sup>[121]</sup> This system was recently applied to furnish 7- and 8-membered cyclic carbonates.<sup>[10c]</sup>



**Scheme 10.** Organocatalytic synthesis of six-membered cyclic carbonates from CO<sub>2</sub> and diol substrates.

The DBU catalyzed mechanism was hypothesised to begin with mono CO<sub>2</sub> insertion into one alcohol to form the carbonate after the deprotonation. Following this, intramolecular attack from the second

alcohol completes the cyclisation process to form the corresponding 6CC. Interestingly, the cyclisation step is ineffective without the addition of tosyl chloride to form a good leaving group, and density functional theory (DFT) studies have corroborated the high energy barrier in the cyclisation step.<sup>[121]</sup> After the successful synthesis of 6CCs, numerous other green CO<sub>2</sub>-based copolymers from renewable feed stocks were explored. Other compounds such as mannopyranose<sup>[122]</sup>, thymidine,<sup>[123]</sup> 2-deoxy-D-ribose,<sup>[124]</sup> and glycosides<sup>[125]</sup> derivatives were coupled directly with CO<sub>2</sub> using organobases to afford cyclic monomers that were polymerised to form novel polycarbonates that have promising biomaterial applications.

In 2016, the first metal-free CO<sub>2</sub>-based polycarbonate synthesis was achieved by activating an epoxide with a strong Lewis acid (triethyl borane) in the presence of organic cation species such as ammonium halides.<sup>[126]</sup> The Lewis acid was crucial to lowering the activation barrier of the epoxide ring-opening to compete with the back-biting of carbonate species. Both PO and CHO were copolymerised with CO<sub>2</sub>, to obtain polycarbonates ( $M_n = 43 \text{ kg}\cdot\text{mol}^{-1}$ ,  $\bar{D}_M = 1.10$ ) with a high carbonate content (99%). More recently, triarylboranes were reported in a metal-free protocol where the selectivity between cyclic carbonate/polycarbonate reaction products could be controlled according to the relative Lewis acidity of the borane species.<sup>[127]</sup> An organocatalyzed approach featuring a binary system composed of 1,3-bis(2-hydroxyhexafluoroisopropyl)benzene and tetrabutylammonium iodide was also effective for CO<sub>2</sub> copolymerization with trimethylene oxide (TMO), a traditionally challenging monomer.<sup>[22a]</sup> An oligocarbonate ( $M_n = 2 \text{ kg}\cdot\text{mol}^{-1}$ ) was obtained after 24h under 10 MPa CO<sub>2</sub> and 130 °C, demonstrating one of the only instances of organocatalyzed CO<sub>2</sub>/TMO copolymerization.

## 1.4. Conclusion and Outlook

The copolymerization of CO<sub>2</sub>/EP offers an efficient approach to sustainable polycarbonates and has accordingly drawn a great deal of attention in recent decades. Industrial scale processes have been applied for these copolymerisations as a result of better catalysts enabling the process to become



more economically viable. In turn, this could facilitate the production of a diverse array of polycarbonates with tuneable thermomechanical properties under increasingly mild conditions. Nevertheless, the current portfolio of non-degradable plastics still remains comparatively inexpensive, but environmental concerns associated with their irresponsible use are drastically increasing. Therefore, it is imperative to continue the development of more sustainable polymers (those from renewable sources and/or possessing biodegradability) and lower the cost of such materials. As it stands, renewable plastics from bio-based monomers and CO<sub>2</sub> are poised to compete with petroleum-derived products. For example, poly (limonene carbonate)<sup>[128]</sup> and 2,5-furandicarboxylic acid (FDCA) (a monomer from biomass waste/CO<sub>2</sub>)<sup>[129]</sup> have led to various methodologies of CO<sub>2</sub> utilisation and shown great promise as robust plastics in the coming future.

The issue of replacing petroleum commodity plastics remains a great challenge for the chemistry community, but producing polycarbonates from CO<sub>2</sub>, and sustainable polymers in general, are still nascent and further improvements will certainly be gained from more efficient catalysts. While few works on the CO<sub>2</sub>-based polycarbonate preparation are addressed by applying heterogeneous catalysts, homogeneous catalytic approaches using organo(metallic) catalysts to convert and valorise CO<sub>2</sub> as a comonomer continue to thrive. Organocatalyzed methods could provide a breakthrough and further drive the production price down while offering an even greener approach. Although both metal- and organic- based catalysts present several respective advantages and viable options for CO<sub>2</sub>-based polymer synthesis, overcoming the sensitivity against contamination (*e.g.* oxygen, moisture), and using air as a CO<sub>2</sub> resource, could allow CO<sub>2</sub>-based fabrication to be carried out on a global industrial scale.

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